

# **Thin Coatings of Polymeric Carbon and Carbon Nanotubes for Corrosion Protection**

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ARDEC: J. Zunino

*2009 US Army Corrosion Summit*



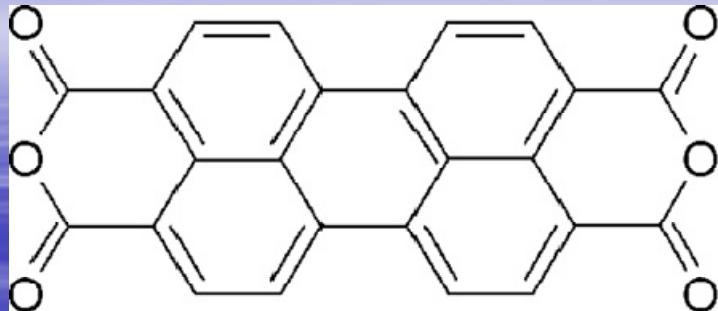
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# Outline of talk

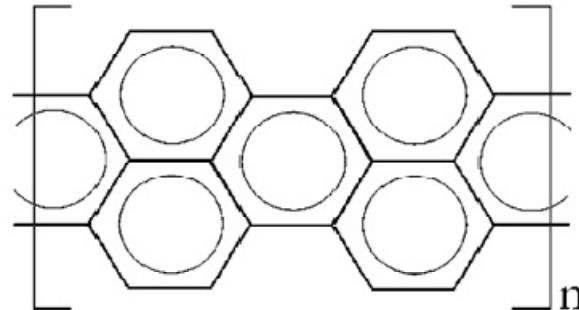
- Introduction – new barrier materials and concepts for corrosion protection
  - Conjugated/conducting polymers
  - Smart-active corrosion protection with carbon nanotube *p-n* junctions
  - Potential corrosion protection in iron-carbon nanotube composites
- Polyperinaphthalene (PPN) results
- Carbon Nanotube approaches and results
- Thermochromic conjugated polymer concepts
- Summary



# Chemical Structures of Coating Materials

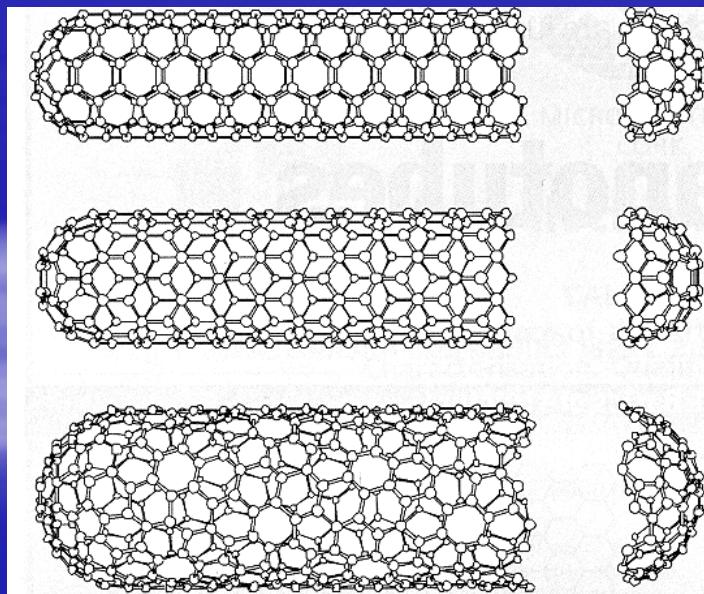


(a)

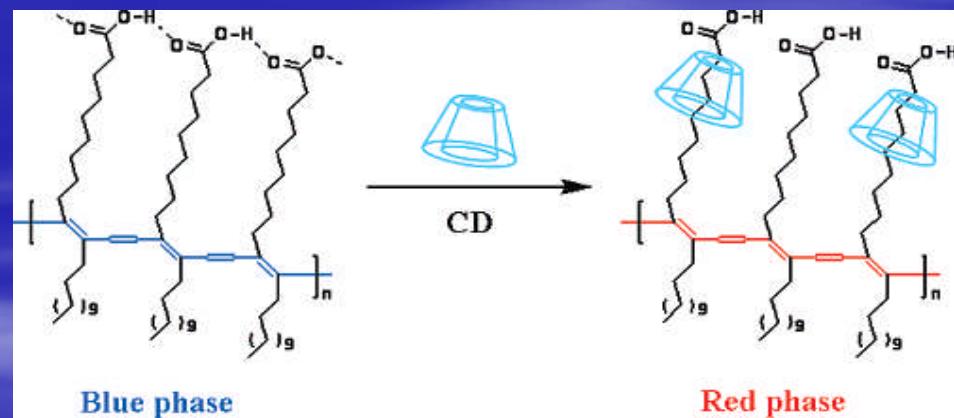


(b)

Polyperinaphthalene (PPN)

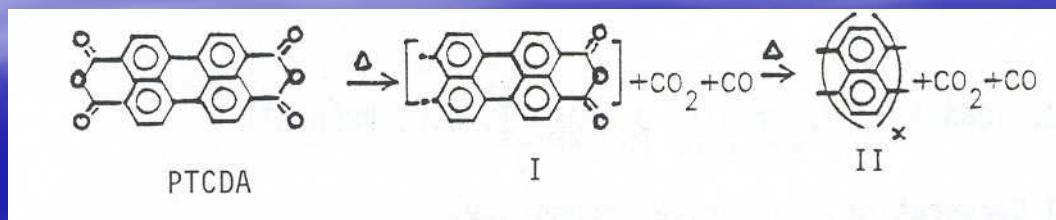
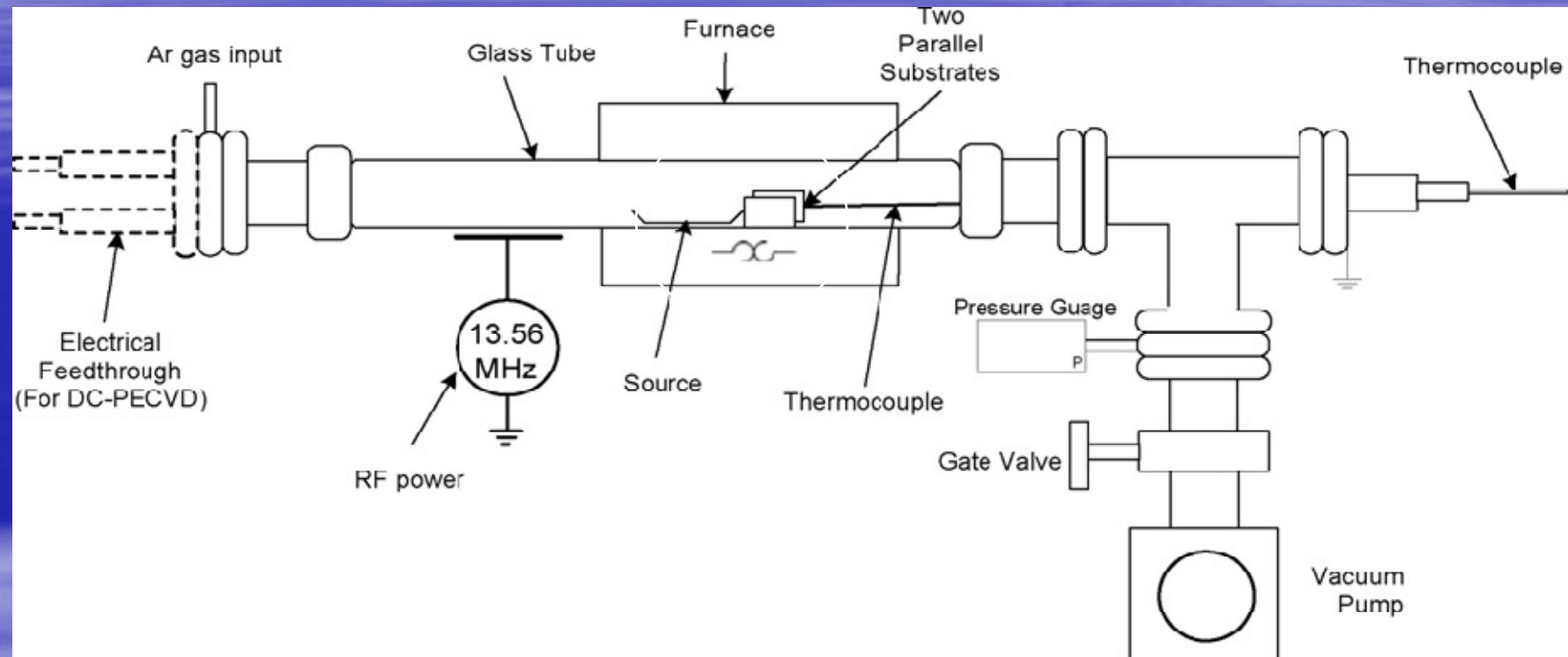


Single wall carbon nanotubes



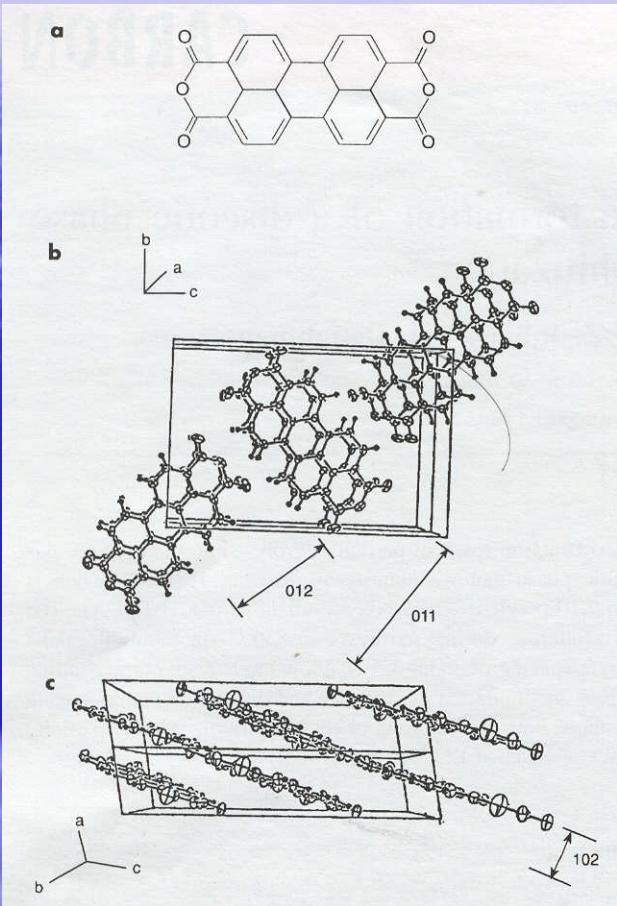
Polydiacetylene:  $\text{CH}_3(\text{CH}_2)_{11}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_8-\text{COOH}$

# Apparatus for Plasma-CVD Synthesis and Deposition of PPN

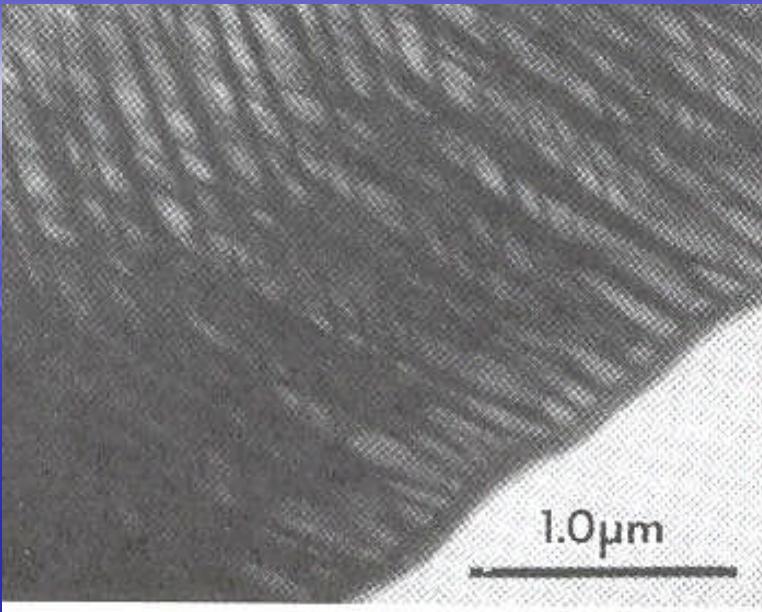


C. Yu, S. C. Wang, M. Sosnowski, and Z. Iqbal, *Synthetic Metals* 158, 425 (2008)

# Transition from PTCDA precursor to PPN

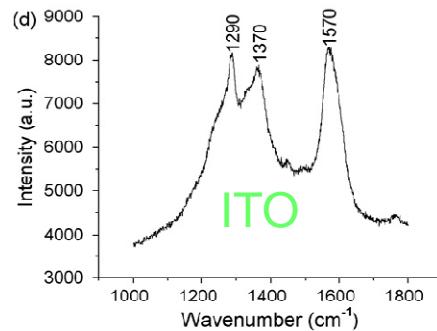
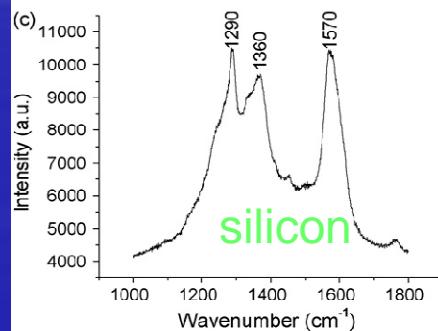
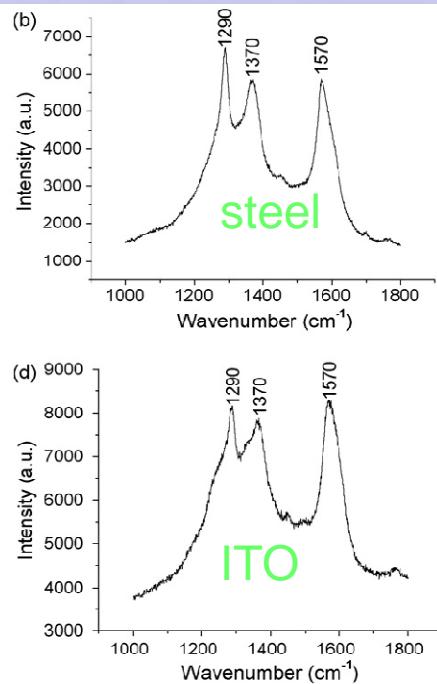
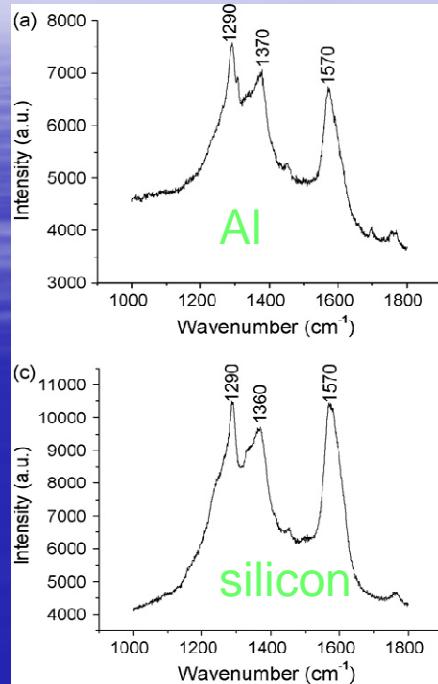


Crystal structure of  
PTCDA precursor

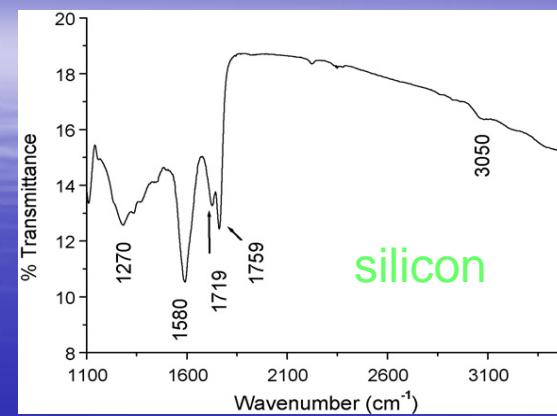


TEM images of PPN

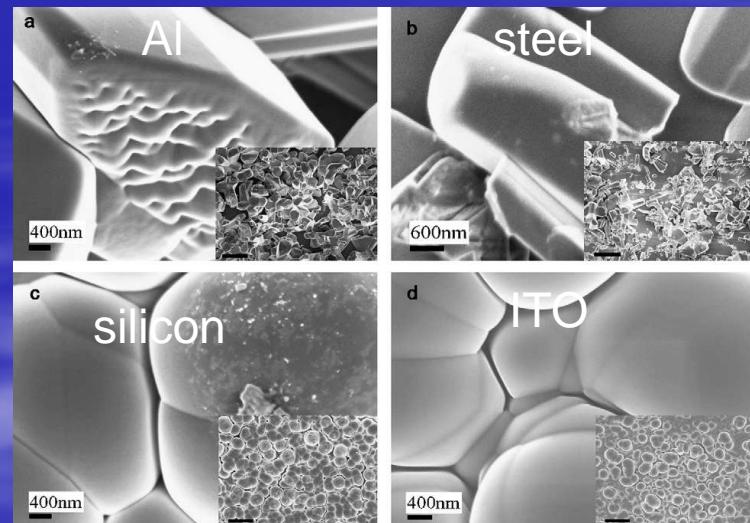
# PPN Coating Characterization



Raman



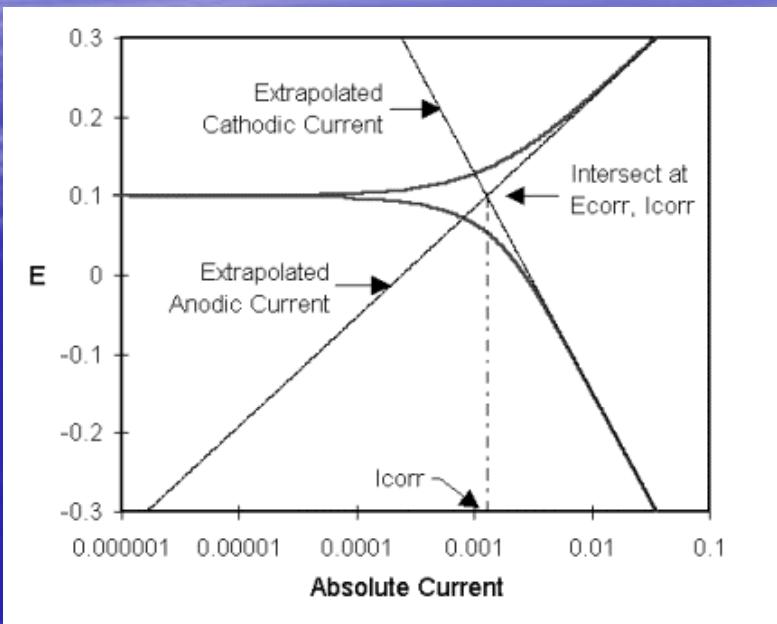
FTIR



SEM on different substrates

C. Yu, S. C. Wang, M. Sosnowski, and Z. Iqbal, *Synthetic Metals* 158, 425 (2008)

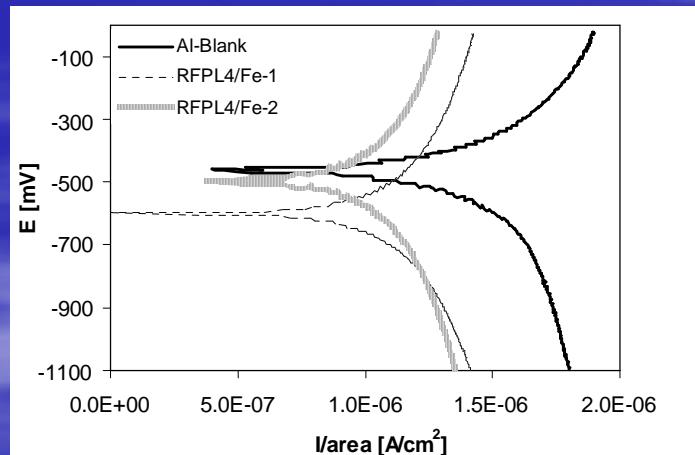
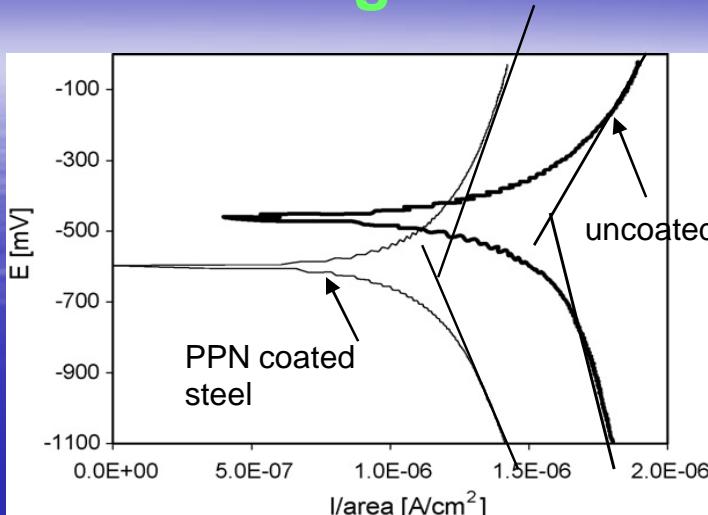
# Potentiodynamic Corrosion Testing Tafel Plots



## Applications:

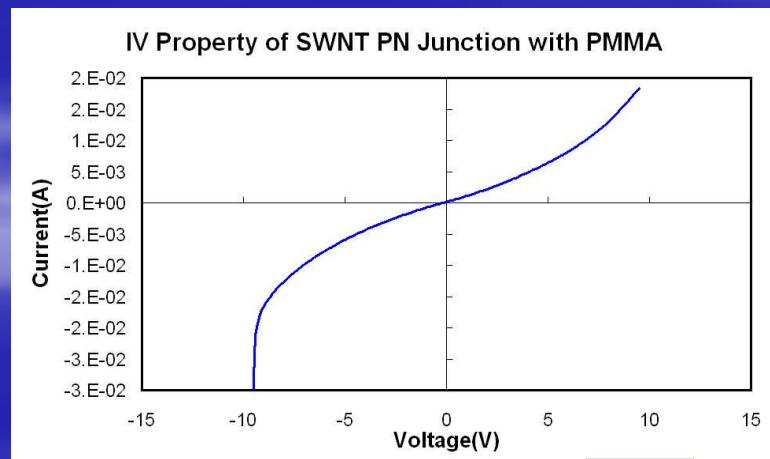
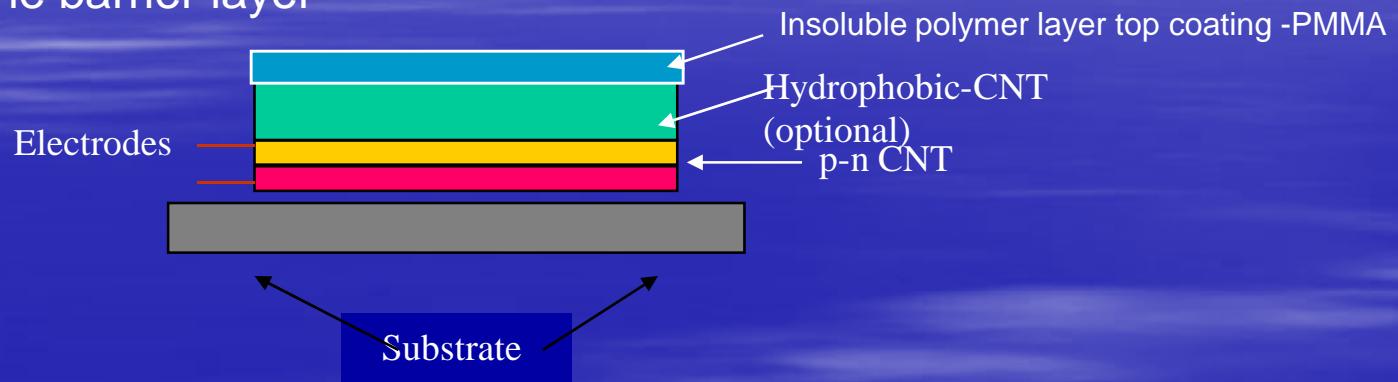
- Corrosion protection for inaccessible device components
- Corrosion protection for fuel cell current collecting bipolar flow-field plates ["Corrosion Resistant Coated Fuel Cell Plate with Graphite Protective Barrier and Method of Making the Same", Z. Iqbal, T. Rehg, J. Guiheen and D. Narasimhan – US Patent 6,864,007 (2005)

Honeywell-GE Power Systems].



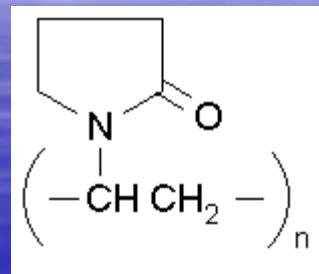
# Multilayer Smart Carbon Nanotube Coating

- Paints of 3 types of carbon nanotubes prepared as paints or inks in polymers
- p-n doped layer functions as a transistor to monitor the health of the coating
- Top layer functionalized with hydrophobic (e.g. fluorine-containing) groups functions as the barrier layer



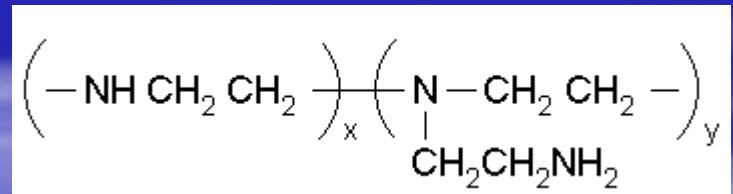
# Carbon Nanotube Functionalization/Doping

## A) *p*-Doping



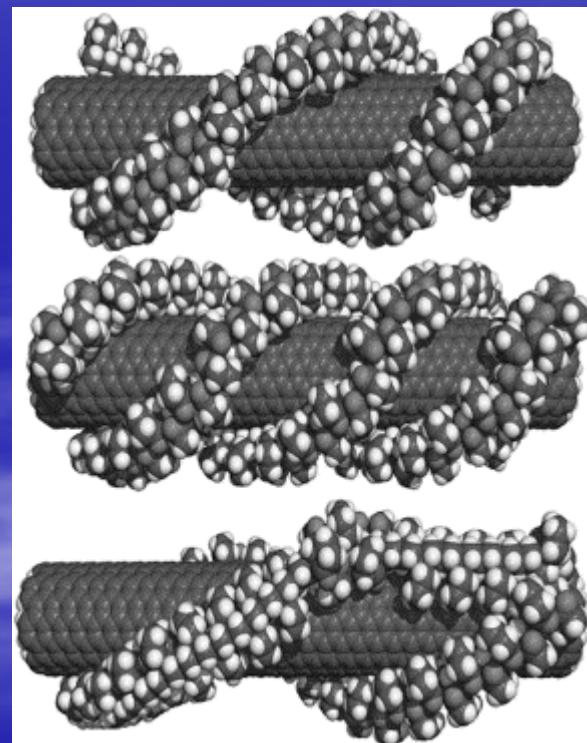
Polyvinylpyrrolidone (PVP)

## B) *n*-Doping

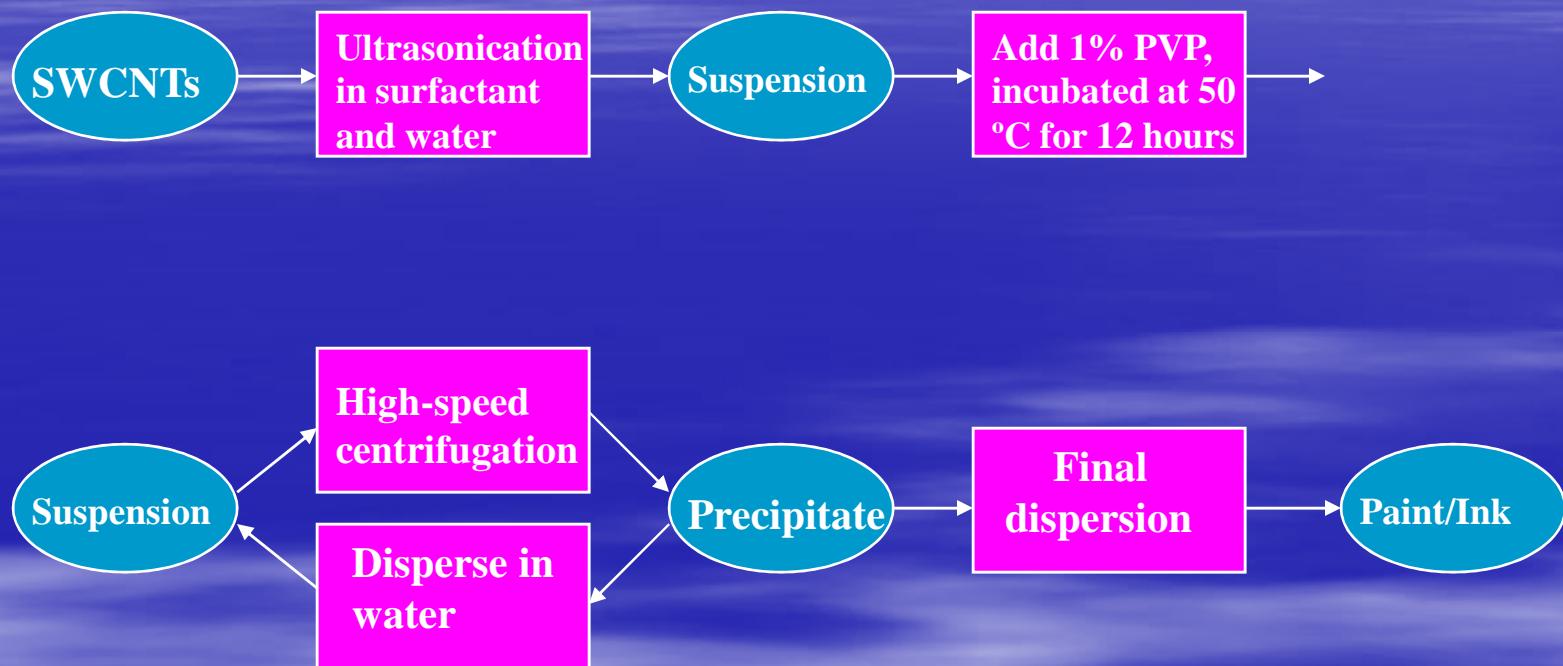


Polyethylenimine  
(PEI)

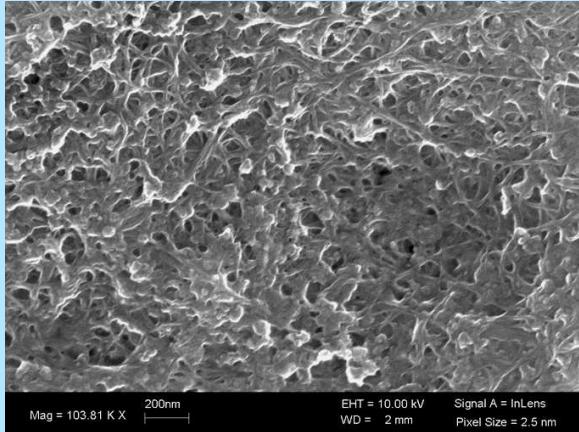
## C) Polymer Wrapping Model



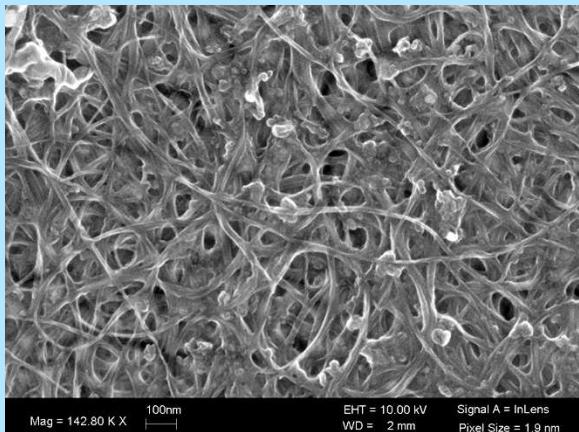
# SWCNT Paint/Ink for Coatings



# Multilayer Smart Carbon Nanotube Coating

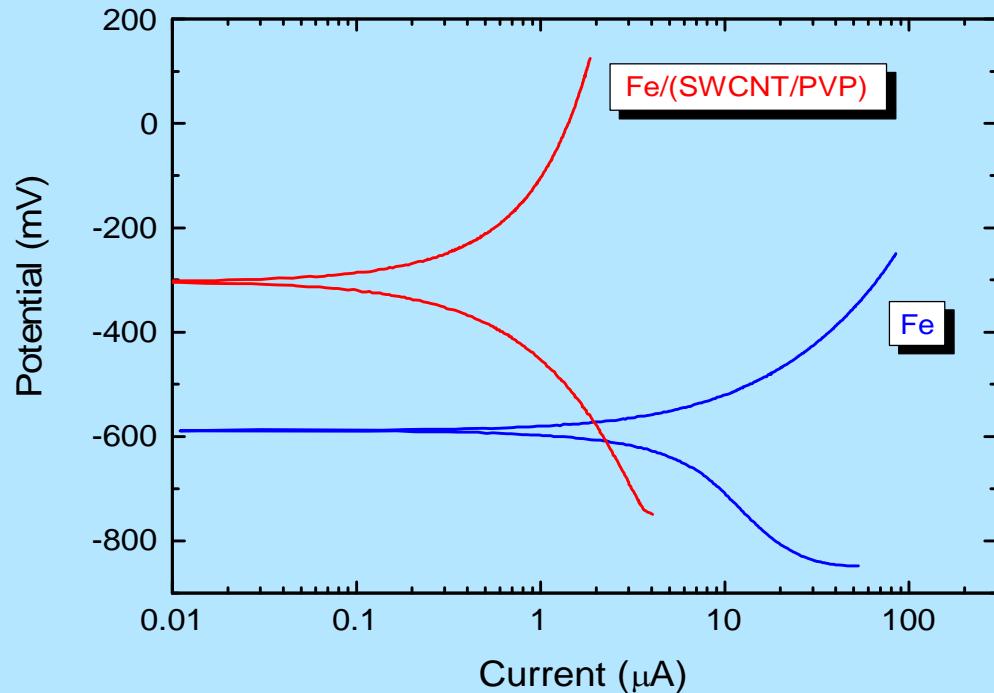


*p*-doped SWCNTs PVP



*n*-doped SWCNTs PEI

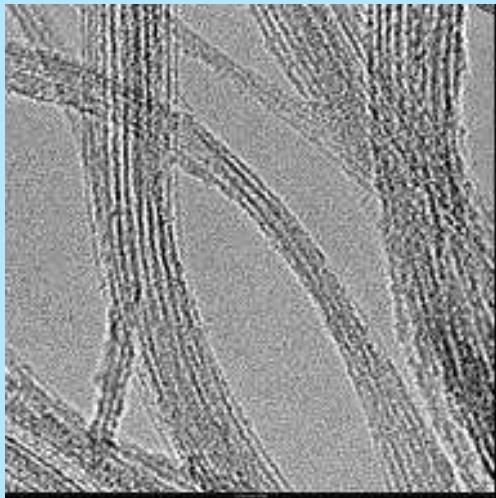
## Tafel Plots of Coated and Uncoated Iron



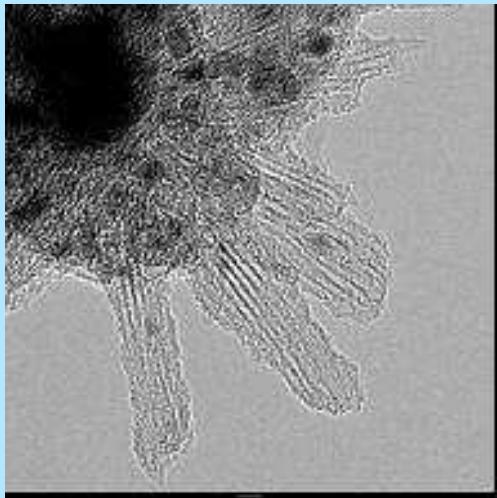
Corrosion current decreases with nanotube coating-  
thus improved corrosion protection

# Multilayer Smart Carbon Nanotube Coating

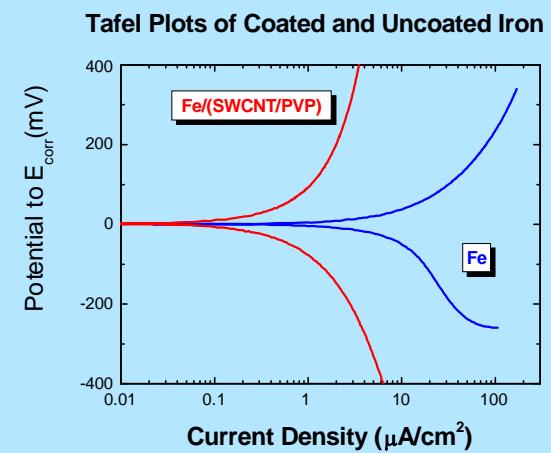
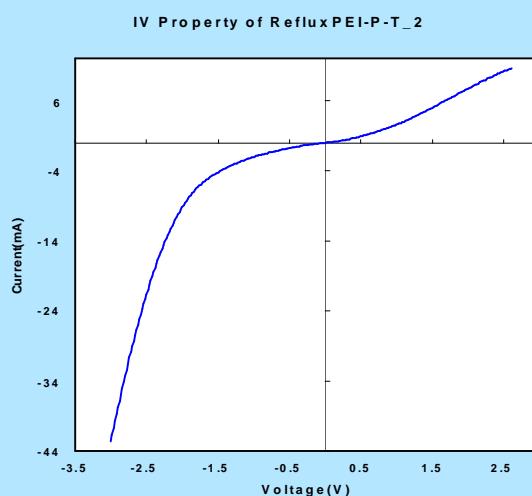
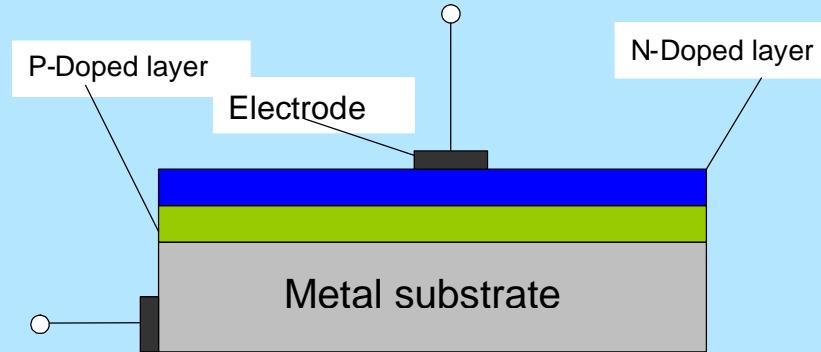
## TEMs



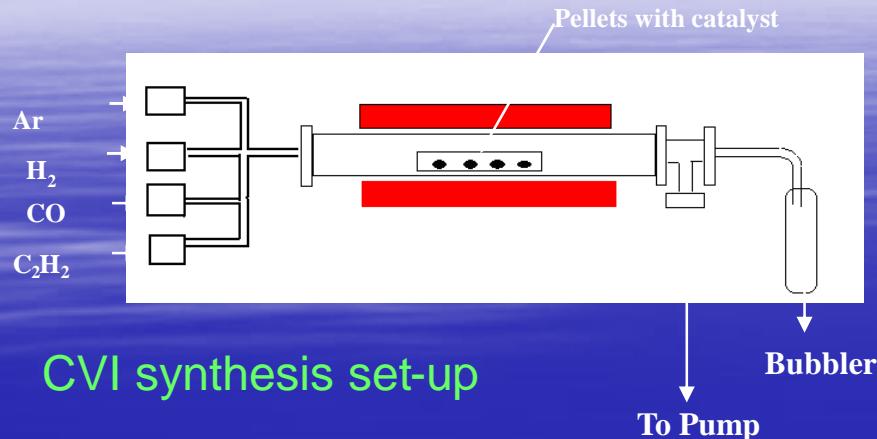
As-prepared SWCNTs



n-doped SWCNTs PEI

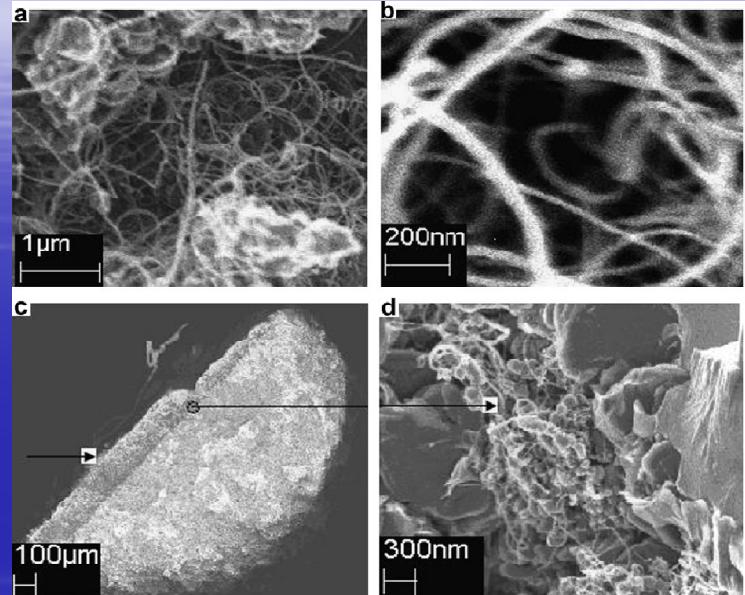


# Potentially corrosion-resistant high strength bulk iron-carbon nanotube composites

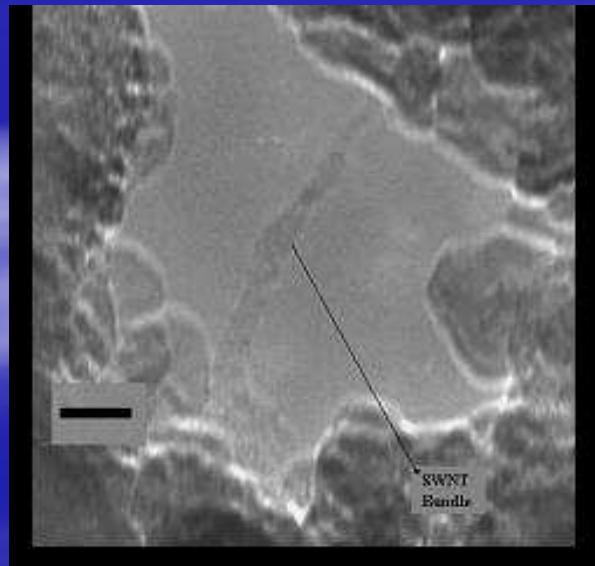


CVI synthesis set-up

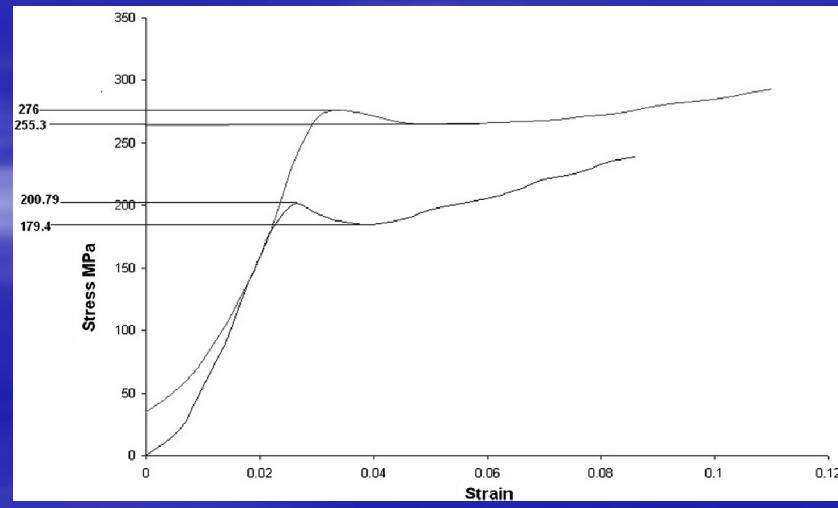
SEM



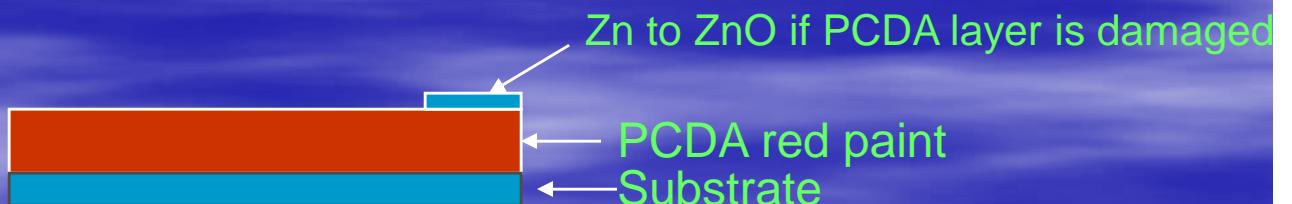
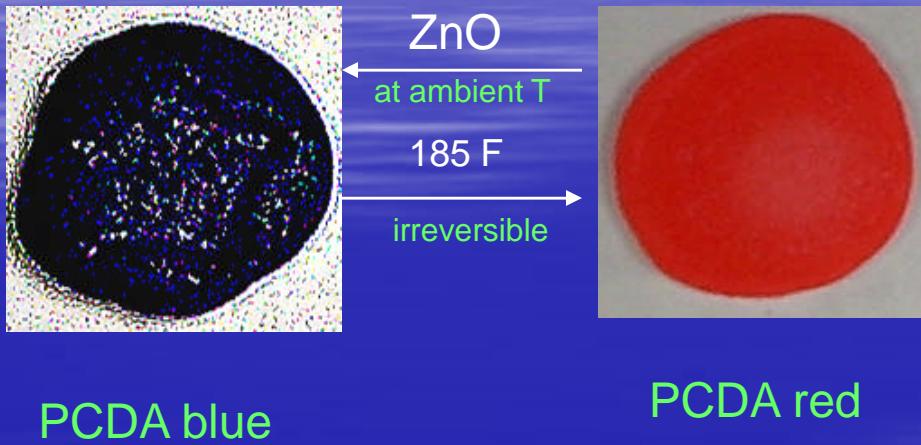
TEM



45% increase in yield strength relative to iron

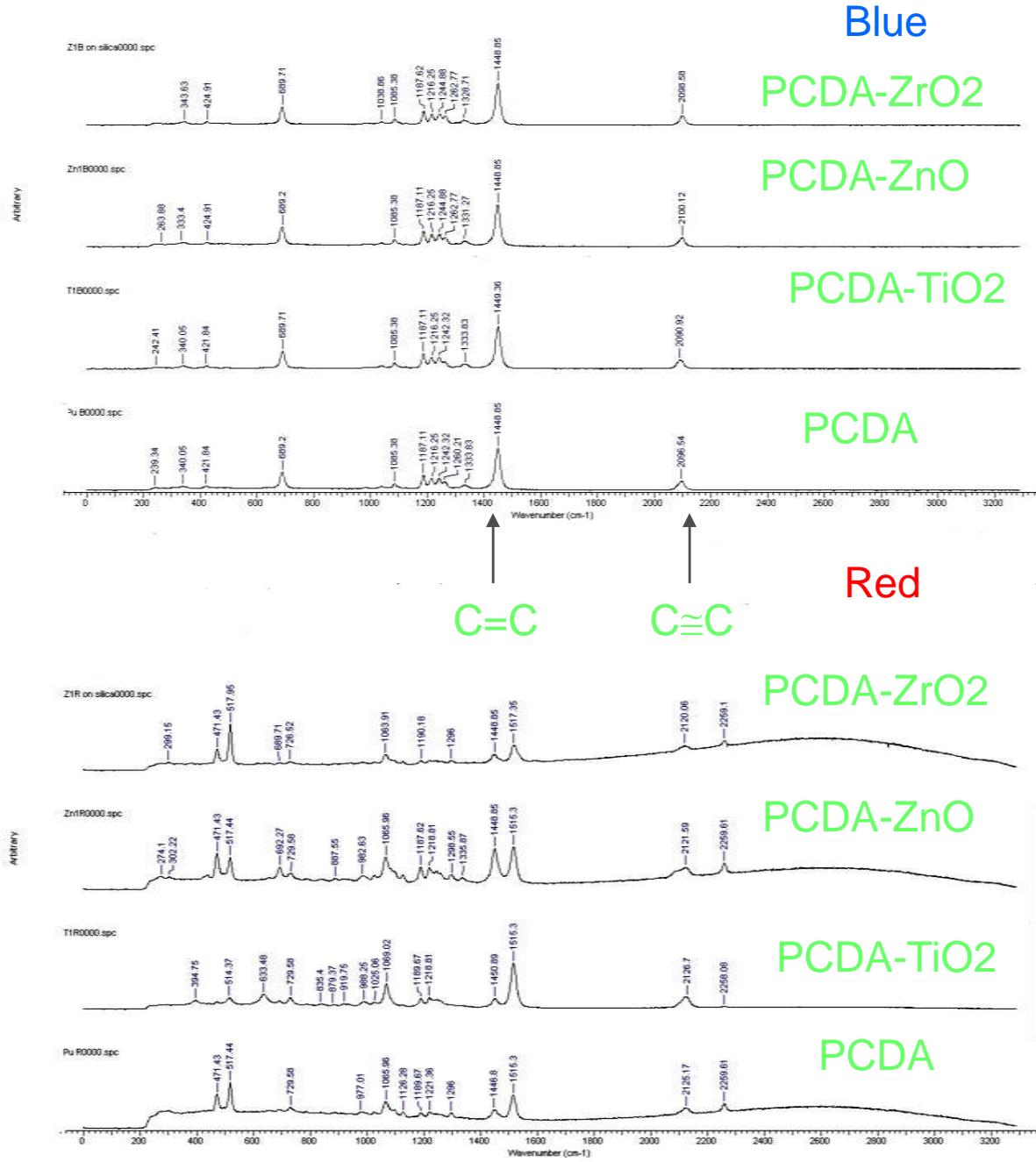


# Multilayer Smart Polydiacetylene Paint Coating



## Monitoring blue and red PCDA phases in presence or absence of ZnO, ZrO<sub>2</sub> and TiO<sub>2</sub> by Raman scattering

Also note: Red phase is highly fluorescent



# Summary

- Three types of nanotechnology-based passive and smart barrier coatings for corrosion protection discussed
  - Plasma-deposited conducting carbon polymer PPN can be used to protect small device or engine components and has been demonstrated to protect PEM fuel cell current collecting bipolar metal plates
  - Carbon nanotube paints/inks can form smart protective coatings via p-n junction layers which can electrically sense coating damage due to corrosion
  - Semiconducting, thermochromic polydiacetylene paints undergo irreversible color changes which can become reversible in the presence of chemical reactions induced by corrosion

